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Process for the coating of conductive articles

The invention relates to a process for the coating of conductive articles in which a base coat or primer, formed by cathodic deposition by the electrophoretic coating process, is provided with a top coat which is crosslinkable by high-energy radiation, the top coat and the base coat located therebelow being cured simultaneously by the high-energy radiation after thermal pre-crosslinking of the base coat.

The curing of base coats formed individually by anodic deposition under the effect of high-energy radiation, in particular of an electron beam, is known from the literature. Thus, in patent AT 301 720 or patent GB 1 207 469, respectively, the DE-OS patent applications published under Nos. 16 21 911 and 20 15 287, or the DE-AS patent application made available for public inspection under No. 17 20 717, mixtures, emulsified in water, of unsaturated polyesters or polymers, which are water-soluble after neutralisation with bases, and copolymerisable monomers are deposited on the anode under the effect of a direct current. The coatings that are obtained are placed below the radiation source and cured after removal, by rinsing, of the adhering material of the bath and optional removal, by blowing, of the drops of water.

Apart from the known drawbacks that anodic coatings have in relation to cathodically deposited base coats, there are other problems with regard to maintaining the stability of the bath, owing to the emulsified monomers and the water content, which is not always uniform, of the films applied, and with regard to the interlayer adhesion, which is almost always lacking, of the other coat applied to a base coat of this type.

The main advantages of curing coatings by high-energy radiation, in particular by an electron beam, consist in the possibility of producing films having excellent surface properties at low crosslinking temperatures, thus obviating the need, compared to coating using coats requiring baking, for relatively long heating and cooling phases. One drawback of coatings crosslinked

by an electron beam is their poor adhesion both to metal substrates and to conventional base coats.

In order to prepare coatings having two or more layers, it would be desirable to combine the two available processes in a highly efficient manner, but for most applications, for example for the mass coating of metal articles such as wheel rims for motor vehicles or other so-called "small parts" in the automotive industry or other sectors.

It has now been found that coatings having very good properties on conductive articles, preferably metal articles, could be obtained by partially crosslinking under the effect of heat a cathodically deposited base coat based on crosslinkable binders, by applying to this layer, which has not completely cured, a top coat which is crosslinkable by high-energy radiation, and by completely curing the top coat and the base coat located therebelow using an electron beam or an equivalent high-energy radiation means.

The present invention accordingly relates to a process for the multilayer coating of conductive articles, characterised in that:

- 1) a base coat, based on a binder which is water-dilutable after neutralisation with acids and crosslinkable by polymerisation, is applied by the electrophoretic coating process to a conductive article connected as a cathode,
- 2) the coated article is crosslinked, optionally after removal, by rinsing with water, of the adhering material from the bath and optionally after removal of the residual water particles, under the effect of heat, to a degree of polymerisation at 10 % below the normal degree of crosslinking,
- 3) a top coat based on a binder which is crosslinkable by high-energy radiation is applied to this base coat by spraying, immersion, flow-coating or rolling, and
- 4) completely curing all coats by high-energy radiation.

The coatings obtained according to the invention are characterised by very good corrosion and stone impact resistance – due in part to the particularly effective adhesion between the base coat and the top coat. This property may be attributed to the fact that above those crosslinking sites of the base coat that are not completely used, the high-energy radiation causes additional securing of the top coat during the curing process.

Binders having in their molecular edifice a sufficient number of polymerisable double bonds, preferably end-of-chain bonds, for the crosslinking process are advantageously used for producing the base coat. Binders of this type for cathodic deposition using the electrophoretic coating process are described, for example, in patents GB 1 551 509 and 1 551 496, and patents AT 343 769, 345 407, 346 987, 346 989, 353 369 and 356 226. Binders of this type are preferably used since, firstly, owing to their end-of-chain double bonds, they produce, during the thermal polymerisation curing process, films having very good resistance properties and, secondly, owing to the remaining polymerisable sites during the incomplete curing process, the subsequent coat is attached.

Nevertheless, it is also possible to adapt conventional cationically depositable systems to the process according to the invention by introducing a minimum amount to the end-of-chain double bonds in such binders. Modifications of this type are described, for example, in patents AT 343 770, 341 771 and 356 226.

The deposition methods using the electrophoretic coating process are known to a person skilled in the art and do not therefore require detailed description. The deposition conditions vary for the individual products or product groups and are indicated in the corresponding documents.

It is, according to the invention, crucial to respect the indicated limits for the degree of crosslinking to be adhered to during the incomplete thermal curing of the base coat applied using the electrophoretic coating process. For obtaining effective interlayer adhesion, it should not be greater than 90 %, and should preferably be between 50 and 90 %, of the maximum degree of crosslinking.

The lower limit for the degree of crosslinking during the incomplete curing process depends on the possibility of curing, by high-energy radiation, the film applied using the electrophoretic coating process, which film takes the same time to dry as the top coat.

In such cases, the degree of crosslinking obtained by thermal polymerisation may also be in the range of from 10 to 60 %.

The baking conditions may, for example, be determined by fixing the resistance to acetone or to methylethylketone. The baking temperatures may be selected between 110 and 190 °C, preferably between 130 and 180 °C. The baking times are between 5 and 30 minutes, depending on the selected temperature and the desired degree of crosslinking. Longer dwell times may, of course, also be selected (although these are not usually allowed in practice).

The top coat is applied in the conventional manner for systems of this type, for example by spraying, immersion, flow-coating or rolling. The top coat may also, if appropriate, consist of a pigment-based paint and a transparent coat applied from above. The corresponding coat systems, which may be crosslinked by high-energy radiation, in particular an electron beam, and the installations used are known from the literature. Corresponding binders are known, for example, from patents AT 323 298, 336 148, 335 023 and 338 944, and the DE-OS patent application published under No. 24 29 627 or patent US 4 164 486. The process according to the invention may be used for coating conductive substrates. The substrates used are conventionally metals, which either are simply degreased or are also phosphatised. The process is particularly suitable for coating vehicle wheel rims.

A better understanding of the invention will be facilitated by the following non-limiting examples. All of the proportions in parts or in percentages refer to units of weight and to solid resin, unless otherwise indicated.

Examples 1 to 11

Under the conditions indicated in the following table, steel plates were coated cathodically in the conventional manner, using the electrophoretic coating process, with a zinc phosphate.

The plates provided with this coating were rinsed with deionised water, and the adhering water was removed by blowing with compressed air. The baking conditions were respectively determined by a preliminary test for determining the resistance to methylethylcetone of a plate subjected to baking at 190 °C for 30 minutes.

The transparent coat was applied by spraying and cured at the exposure rate indicated in the table.

Materials used in the examples

1. Base coat deposited cathodically using the electrophoretic coating process, known as the KETL base coat

1. Binder

W 1: patent AT 342 169, Example 2

W 2: patent AT 342 169, Example 6

W 3: (a) 380 g of a bisphenol A-based epoxy resin (epoxy equivalent: approximately 190) and 564 g of a hemiester consisting of tetrahydrophthalic anhydride and hydroxyethyl methacrylate were reacted, in 80 % solution, in ethylene glycol monoethyl ether acetate at 105 °C until an acid value of less than 5 mg KOH/g was obtained. 364 g of a basic monoisocyanate (consisting of equimolar amounts of toluene diisocyanate and diethylethanolamine (80 % in ethylene glycol monoethyl ether acetate)) were then added and the mixture was allowed to react for two hours at 60 to 70 °C. The product was diluted with ethylene glycol monoethylether until 70 % by weight of solids were obtained.

b) 380 g of the epoxy resin used in (a) were reacted with 210g of diethanolamine for 3 hours at 130 °C. The mixture was then diluted with ethylene glycol momoethylether acetate until 70 % by weight of solids were obtained. The mixture was reacted, at 60 to 70 °C for 2 hours, with 380 g of an unsaturated monoisocyanate (consisting of equimolar amounts of toluene diisocyanate and hydroxyethyl methacrylate). The product was diluted with ethylene glycol monoethylether acetate until 70 % by weight of solids were obtained.

c) 80 g of product (a) and 20 g of product (b) were mixed, W 3 being used as the binder. Formic acid was used for the purposes of neutralisation during the production of the cathodic deposition bath using the electrophoretic deposition process.

W4 : (a) 380 g of the epoxy resin used in W 3 (a) were reacted, in a solution of ethylene glycol monoethyletheracetate at 100 to 110 °C, with 100 g of acrylic acid until an acid value of almost 0 was obtained. After the addition of 329 g of a basic monoisocyanate (consisting of the equimolar amounts of toluene diisocyanate and dimethylethanolamine in 80 % solution in ethylene glycol acetate), the mixture was reacted at 60 to 70 °C until an NCO value of almost 0 was obtained. The product was diluted with ethylene glycol monoethylether acetate until a 70 % solids content was obtained.

(b) 380 g of the epoxy resin used in (a) were added slowly, in a solution of ethylene glycol monoethylether acetate at 90 to 120 °C, to 210 g of diethanolamine, and the mixture was reacted for 1 hour at 150 °C. The mixture was then reacted, at 60 to 70 °C, with 380 g of an unsaturated monoisocyanate (see W 3 (b)) until an NCO value of 0 was obtained, and the product was diluted with ethylene glycol monoethylether acetate until a solids content of 70 % by weight was obtained.

(c) 250 g of a bisphenol A-based epoxy resin (EG = approximately 500), 1,300 g of a phenolic novolak-based epoxy resin (EG = 170 to 180), 742 g of a tetrahydrophthalic anhydride hemiester in 80 % solution in MIBK and N-2-hydroxypropyl-5-methyloxazolidine, 80 g of diethylaminopropylamine, 73 g of diethylamine, 660 g of an o-phthalic anhydride hemiester, hydroxyethyl methacrylate and 168 g of tallol fatty acid with ethylene glycol monoethylether until a solids content of 60 % by weight was obtained. The mixture was reacted at 75 °C until an acid value of less than 5 mg of KOH/g was obtained.

W5: patent AT 348 634, Example 4.

2. Production of the coat

Coat A (consisting of W 1 to W 3 and W 5): the resins were partially neutralised with the necessary amount of acid (i.e. for W 1: 3.6 g of acetic acid; for W 2: 3.8 g of acetic acid; for W 3: 4.0 g of formic acid; for W 5: 3.8 g of acetic acid; for 100 g of solid resin in each case). A coating concentrate containing, for 100 g of solid resin, 14.6 g of titanium dioxide, 9.4 g of aluminium silicate pigment, 2.5 g of lead silicate, 2.5 g of strontium chromate and 1 g of carbon black were produced from this resin solution using a tricylinder. The concentrate was diluted with dionised water and a 10 % solids content was obtained.

Coat b, based on component W 4 (c), which was neutralised with 30 millimoles of acetic acid, 100 g of solid resin; a coating concentrate containing, for 100 g of solid resin, 23 g of aluminium silicate pigment, 24 g of titanium dioxide, 2 g of lead silicate pigment, 1 g of carbon black and 10 g of dionised water, was produced using a bead mill.

An amount of coating concentrate corresponding to 15 g of solid resin was added to a mixture consisting of 70 g (solid resin) of the component W 4 (b), which was neutralised with 60 millimoles of acetic acid/100 g of solid resin. After thorough mixing, the coat was diluted until a solids content of 12 % by weight was obtained.

II. Coat cured by electron beam

1. Binder

E 1 : 400 g of the epoxy resin used in W 1 were reacted with 144 g of acrylic acid, at 110 °C, until an acid value of less than 3 mg of KOH/g was obtained, and were diluted with hexanediol diacrylate until a solids content of 70 % was obtained.

E 2: 1,000 g of a saturated polyester obtained from 102 g of adipic acid, 16 g of neopentyl glycol and 121 g of trimethylolpropane were reacted with 870 g of an unsaturated monisocyanate (consisting of equimolar amounts of toluene diisocyanate and hydroxyethyl acrylate), at 60 to 70 °C, in 80 % solution in hexanediol diacrylate, until an NCO value of

almost 0 was obtained, and were diluted with hexanediol diacrylate until a 70 % solids content was obtained.

E3: 400 g of the epoxy resin used in W 1 were reacted with 564 g of a tetrahydrophthalic acid anhydride and hydroxyethyl methacrylate hemiester, at 110 °C, until an acid value of less than 5 mg of KOH/g was obtained, and were diluted with a 1/1 mixture of neopentyl glycol diacrylate and hydroxyethyl acrylate until a 70 % solids content was obtained.

E4: 400 g of the epoxy resin used in W 1 were reacted with 210 g of diethanolamine for 3 hours at 130 °C. The resultant product was diluted with hexanediol diacrylate until an 80 % solids content was obtained, then reacted with 725 g of the unsaturated monoisocyanate used in E 2, at 60 to 70 °C, until an MCO value of almost 0 was obtained. The product was diluted with hydroxypropyl acrylate until a 70 % solids content was obtained.

2. Production of the coat

100 g of solid resin were diluted with a 3/1 mixture of tetraethylene glycol diacrylate and 2-hydroxypropyl acrylate until a viscosity of 80" (DIN 53 211, 23 °C) was obtained. A silvery paint was produced by adding 23 g of aluminium paste and a levelling agent while stirring.

III. Description of the control method

1. Control of the degree of crosslinking of the KETL base coat. Curves showing the dependence of the resistance to methylethylcetone on the baking temperature or the baking time, respectively. The "degree of crosslinking" designates the percentage of the resistance to solvents (as a function of time) of the plate subjected to the test. A coating baked for 30 minutes at 90 °C is assumed to have a resistance to solvents of 100 %.

2. Hardness: to Standard DIN 53 157 (König)

3. Adhesion: the degree of adhesion between the intermediate layers was measured by the BRAIVE scratch test using the CLEMEN apparatus (OCF 55 model). The table indicates the weight at which the coat structure had not yet deteriorated using this method. When, in the comparative tests, the weight was increased by 100 g, the top coat became detached from the base coat. In the case of the coat structures according to the invention, the entire coat structure was destroyed once the indicated values had been exceeded. Detachment of the top coat alone did not occur in any instance.

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Example	KETL BASE COAT				ESH TOP COAT		CONTROL	
	RESIN/PAINT	BAKING CONDITIONS			RESIN	Exposure rate Mrad	Hardness s	Adhesion g
		Temp °C	Time Min	Degree of crosslinking/%				
1	W1/a	160	15	55	E1	3	230	1400
2	W3/a	140	25	25	E2	3	190	1500
3	W2/a	180	10	55	E3	3	220	1200
3 a	W2/a	190	30	100	E3	3	240	400 COMPARISON
4	W4/b	180	10	75	E4	3	240	1300
5	W5/a	150	20	45	E2	2.5	180	1200
6	W5/a	170	30	85	E2	2.5	200	1000
6 a	W5/a	190	30	100	E2	2.5	210	300 COMPARISON
7	W4/b	150	25	40	E2	2.5	180	1500
8	W5/a	160	15	50	E1	3	230	1400
9	W2/a	160	15	55	E4	3	235	1400
10	W2/a	180	10	65	E1	3	220	1200
11	W1/a	180	15	80	E3	4	240	1100
12	W3/a	130	20	15	E3	4	245	1400
12 a	W3/a	190	30	100	E3	4	240	600 COMPARISON

Claims

1. Process for the multilayer coating of conductive articles, characterised in that:
 - 1) a base coat, based on a binder which is water-dilutable after neutralisation with acids and crosslinkable by polymerisation, is applied by the electrophoretic coating process to a conductive article connected as a cathode,
 - 2) the coated article is crosslinked, optionally after removal, by rinsing with water, of the adhering material from the bath and optionally after removal of the residual water particles, under the effect of heat, to a degree of polymerisation at 10 % below the normal degree of crosslinking,
 - 3) a top coat based on binder which is crosslinkable by high-energy radiation is applied to this base coat by spraying, immersion, flow-coating or rolling, and
 - 4) completely curing all coats by high-energy radiation.
2. Process according to claim 1, characterised in that the base coat is crosslinked to a degree of crosslinking of between 50 and 90 %.
3. Process according to claim 1, characterised in that the base coat is crosslinked thermally using binders, which are at least partially crosslinkable by high-energy radiation, to a degree of crosslinking of between 20 and 90 %, preferably between 20 and 80 %.
4. Process according to any one of claims 1 to 3, characterised in that the high-energy radiation used is in the form of an electron beam.
5. Process according to any one of claims 1 to 4, characterised in that the base coat used is in the form of binders having at least 0.2, preferably more than 0.5, end-of-chain double bonds per 1,000 units of molecular weight.